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(1 January 1979 through 31 December 1979)

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A program was started on the synthesis and characterization of energetic azido compounds as potential ingredients for advanced propellant and explosive systems. Initially, a series of mono-azidoalkanes and diazidoalkanes were prepared to compare the molecular structure of these compounds with their impact sensitivity. All of the mono-azidoalkanes were insensitive to impact. The di-azidoalkanes gave varying results, depending on the structure. The effect of molecular structure on the impact sensitivity of azido compounds was dramatically illustrated

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20. ABSTRACT (continued)

by comparing the structure and sensitivity of 1,3-diazidopropane (impact sensitivity <5 in.-lb) and 2,2-bis(azidomethyl) propane (impact sensitivity >250 in.-lb).

Two new energetic azido monomers were prepared. These included 3,3-bis(azidomethyl) oxetane (BAMO) and 3-azido-2,2-dinitropropyl glycidyl ether. BAMO was readily prepared in a one-step reaction from the commercially available 3,3-bis(chloromethyl) oxetane and sodium azide. The initial polymerization work was concentrated on BAMO because of its ease of preparation and its attractive properties (d^{25}=1.22g/cc, ΔH_f = +102 kcal/mole. BAMO was successfully polymerized to give hydroxy-terminated prepolymers with weight average molecular weights in the 2000 to 3000 range and functionalities of 2.8 to 3.0. Preliminary curing studies on these prepolymers gave tough cured gumstocks.

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FOREWORD

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ENERGETIC AZIDO COMPOUNDS

INTRODUCTION

Certain classes of azido compounds have been well known for many years in the explosive industry. These include materials such as lead azide and cyanuric azide, whose extreme sensitivity has made them useful as initiators. Because of this sensitivity property, the exploration and use of azido compounds has been limited. However, it should be recognized that the sensitivity of azides is directly related to their structure. For example, lead azide, with a covalent linkage, is a primary initiator while sodium azide, with an ionic linkage, is completely insensitive. Organic azides in which the azido group is linked to an unsaturated carbon (e.g., cyanuric triazide) are very sensitive. That is not to say that saturated organic azides would also be very sensitive.

The most attractive feature of azide compounds is their high heats of formation. The azido group contributes a positive heat of formation of about 85 kcal/unit. This high contribution of the azido group to the heat of formation is most clearly evident from a comparison of ethanol and 2-azidoethanol, $N_3CH_2CH_2OH$. The heat of formation of ethanol is -66.3 kcal/mole, while 2-azidoethanol has a heat of formation of +22.5 kcal/mole. Thus, the energy content of azido compounds is readily evident.

Energetic azido compounds have outstanding potential for the development of advanced propellant and explosive systems. The key to success is the tailoring of the molecular configuration of the azido groups so as to achieve high energy without the penalty of high sensitivity and poor thermal stability. To adequately exploit the full potential of these energetic compounds, a systematic correlation between the molecular configuration of the azido groups and the physical properties of the resulting compounds is required. To achieve this goal, a basic program on the synthesis and evaluation of the different types of azido compounds was initiated. The areas that were to be studied included:

1. Synthesis of various types of aliphatic azido compounds which would include primary, secondary and tertiary mono-azides as well as vicinal, α, ω-, and gem-diazides

2. Characterization of the synthesized compounds and evaluation of their sensitivity and thermal stability

3. Correlation of the structure of the azido compounds with physical properties

In the fifth month of the program, at the direction of the Scientific Officer, the emphasis of the program was shifted from the synthesis and characterization of azido alkanes to the synthesis and characterization of azido monomers and polymers.

DISCUSSION

Synthesis and Characterization of Azidoalkanes

The method used to prepare the azidoalkanes was via the Sn_2 reaction of sodium azide on the corresponding alkyl halide in dimethylformamide solvent.

$$RX + NaN_3 \xrightarrow{DMF} RN_3 + NaX$$

All of the materials were characterized by boiling point, index of refraction, density, infrared spectra, gas chromatography, and impact sensitivities. In every case the materials exceed 99% purity. Both mono-azidoalkanes and di-azido-alkanes were prepared. The mono-azidoalkanes included the homologous series of 1-azidopropane through 1-azidohexane, as well as azidocyclohexane. The di-azido-alkanes included 1,2-diazidopropane, 1,3-diazidopropane, 1,4-diazidobutane, 2,3-diazido-1-propanol, and 2,2-bis(azidomethyl) propane.

These materials were prepared in sufficient quantity to characterize their physi-cal properties. All of the compounds were purified by distillation, showing good thermal stability. Purity by gas chromatographic analysis was greater than 99% in all cases. The determination of the impact sensitivities of the azido com-pounds gave some surprising results. All of the mono-azidoalkanes were insen-sitive, with impact sensitivities greater than 250 in.-lb. Trimethyolethane trinitrate (TMETN), a standard energetic plasticizer for propellants and explosives, was used as a control and had an impact sensitivity of 30 in.-lb.

The di-azidoalkanes gave varying results, depending on the structure. 1,2-diazido-propane and 1,3-diazido-propane were extremely sensitive, with impact sensitivities less than 5 in.-lb. On the other hand, 1,4-diazidobutane, where the azido groups were separated by an additional carbon atom, had only a moderate sensitivity of 57 in.-lb. 2,2-bis(Azidomethyl) propane was insensitive, with an impact sensitivity greater than 250 in.-lb. The effect of molecular structure on the impact sensitivity of azido compounds was dramatically illustrated by comparing the structure and sensitivity of 1,3-diazidopropane and 2,2-bis(azidomethyl) propane:

$$
\begin{array}{cc}
\overset{\displaystyle ?}{\underset{\displaystyle H}{\text{N}_3\text{CH}_2\text{CCH}_2\text{N}_3}} &
\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\text{N}_3\text{CH}_2\text{CCH}_2\text{N}_3}}
\end{array}
$$
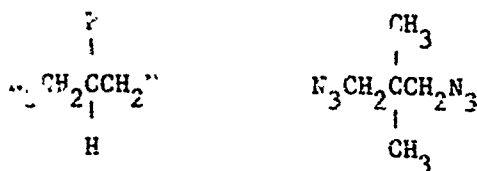
Impact sensitivity

(in.-lb)   <5   >250

The properties of the mono-azidoalkanes and di-azidoalkanes are summarized in Tables 1 and 2, respectively.

Synthesis of Azido Monomers

At the direction of the project officer, the emphasis of the program was shifted to the synthesis of energetic azido monomers. Work was directed to the synthesis of both azido oxetanes and azido nitro epoxides.

Azido Oxetanes. 3,3-bis(Azidomethyl) oxetane (BAMO) was prepared by the reaction of 3,3-bis(chloromethyl) oxetane and sodium azide in dimethylformamide:

$$
\begin{array}{ccc}
\begin{array}{l} CH_2 - C(CH_2Cl)_2 \\ | \qquad | \\ O \ —— \ CH_2 \end{array}
& \xrightarrow[\text{DMF}]{\text{NaN}_3} &
\begin{array}{l} CH_2 - C(CH_2N_3)_2 \\ | \qquad | \\ O \ —— \ CH_2 \end{array}
\end{array}
$$

BAMO

This new energetic monomer is a colorless liquid, boiling point 67 C/0.25mm, n^{25}D 1.5051, d^{25} 1.27. It has a calculated heat of formation of +102 kcal/mole.

TABLE 1. PROPERTIES OF MONO-AZIDOALKANES
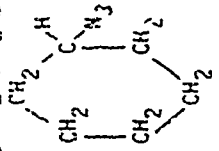
Compound	Structure	Boiling Point	Purity	n_{23}^{25}	Density g/cc (24 C)	Impact Sensitivity in.-lb., 50% fire
1-Azidopropane	$CH_3CH_2CH_2N_3$	73-4 C/ATM	99.8%	1.4093	0.87	>250
2-Azidopropane	$CH_3CH(N_3)CH_3$	63-4 C/ATM	99.5%	1.3986	0.85	>250
1-Azidobutane	$CH_3CH_2CH_2CH_2N_3$	105-6 C/ATM	99.8%	1.4180	0.87	>250
2-Azidobutane	$CH_3CH_2CH(N_3)CH_3$	94-5 C/ATM	99.1%	1.4136	0.86	>250
1-Azidopentane	$CH_3(CH_2)_3CH_2N_3$	89-91 C/128 mm	99.3%	1.4243	0.87	>250
1-Azidohexane	$CH_3(CH_2)_4CH_2N_3$	85 C/62 mm	99.5%	1.4295	0.86	>250
Azidocyclohexane					0.97	>250
TMETN (Control)						30

TABLE 2. PROPERTIES OF DI-AZIDOALKANES

Compound	Structure	Boiling Point	Purity	n_{25}^D	Density g/cc (25 C)	Impact Sensitivity in.-lb. 50% fire
1,2-Diazidopropane	$N_3CH_2CHN_3CH_3$	60-1 C/16 mm	>99%	1.4701	1.09	<5
1,3-Diazidopropane	$N_3CH_2CH_2CH_2N_3$	76-7 C/19 mm	>99%	1.4780	1.11	<5
1,4-Diazidobutane	$N_3CH_2CH_2CH_2CH_2N_3$	42-4 C/0.1 mm	>99%	1.4747	1.07	57
2,3-Diazido-1-propanol	$N_3CH_2CH(N_3)CH_2OH$	71 C/0.1 mm	>99%	1.5058	1.26	7.5
2,2-bis(Azidomethyl)-propane	$CH_3C(CH_2N_3)_2CH_3$	77-8 C/15 mm	>99%	1.4695	1.03	>250
TMETN (Control)						30

<u>Azido Nitro Epoxides.</u> 3-Azido-2,2-dinitropropyl glycidyl ether was prepared by the sequence of reactions shown below:

$$CH_3C(NO_2)_3 \xrightarrow{KOH} [CH_2=C(NO_2)_2]_2 \xrightarrow[HOCH_2CH=CH_2]{KOH} KC(NO_2)_2CH_2OCH_2CH=CH_2$$

$$I$$

$$\xrightarrow[HOAc]{CH_2O} HOCH_2C(NO_2)_2CH_2OCH_2CH=CH_2 \xrightarrow{TsOCl} TsOCH_2C(NO_2)_2CH_2OCH_2CH=CH_2$$

$$II \qquad\qquad\qquad III$$

$$\xrightarrow{NaN_3} N_3CH_2C(NO_2)_2CH_2OCH_2CH=CH_2 \xrightarrow{CF_3CO_3H} N_3CH_2C(NO_2)_2CH_2OCH_2\underset{O}{\overset{}{CHCH_2}}$$

$$IV \qquad\qquad\qquad V$$
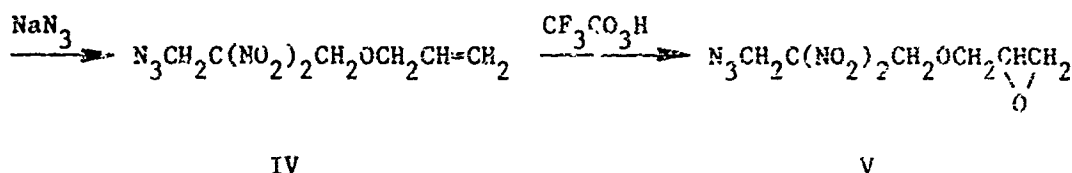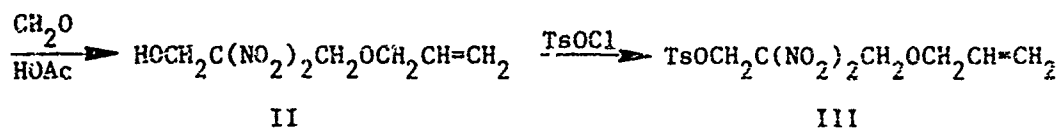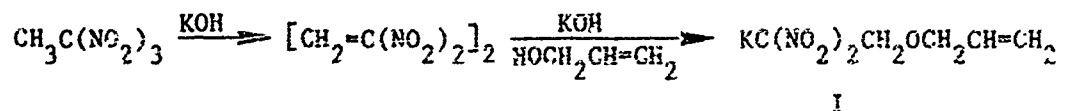
The initial step utilized the dinitroethylation reaction*, which consisted of reacting 1,1,1-trinitroethane with a solution of potassium hydroxide in allyl alcohol to give the potassium salt of allyl 2,2-dinitroethyl allyl ether (I) via the intermediate 1,1-dinitroethylene. Treating of I with aqueous formaldehyde gave 3-hydroxy-2,2-dinitropropyl allyl ether (II), which was converted to the tosylate derivative (III). Reaction of III with sodium azide gave 3-azido-2,2-dinitropropyl allyl ether (IV). Epoxidation of IV with peroxytrifluoroacetic acid yielded the desired 3-azido-2,2-dinitropropyl glycidyl ether (V). Compound V is a liquid with a calculated heat of formation of -33 kcal/mole.

<u>Experimental Section</u>

<u>1-Azidobutane.</u> The preparation of 1-azidobutane is given as typical for the azidoalkanes. A mixture of 54.8g (0.4 m) of 1-bromobutane, 28.6g (0.44 m) of sodium azide, and 200 ml of dimethylformamide was heated with stirring at 90 to 95 C for 20 hours. The reaction mixture was cooled to ambient temperature, poured into two liters of water, and extracted with 150 ml of methylene chloride. The organic layer was separated, washed with 7 x 250 ml of water, and concentrated. The residue was distilled to give 25.1g (63%) of colorless liquid, boiling point 105 to 106 C, $n_{25}D$ 1.4180.

*Frankel, M. B., <u>J. Org. Chem.</u>, 23, 813 (1953).

<u>3,3-bis(Azidomethyl) oxetane</u>. A mixture of 59.5g (0.38m) of distilled 3,3-bis (chloromethyl) oxetane, 54.3g (0.84m) of sodium azide, and 200 ml of dimethylformamide was heated at 90 to 100 C for 2 hours. The reaction mixture was cooled to ambient temperature, poured into one liter of water, and extracted with 200 ml of methylene chloride. The methylene chloride extract was washed twice with 500 ml portions of water, dried over anhydrous sodium sulfate, and concentrated. The resultant pale yellow oil was distilled to give 48.3g (76%) of colorless liquid, boiling point 79 to 81 C/0.4mm, $n_{25}D$ 1.5054.

<u>3-Hydroxy-2,2-dinitropropyl Allyl Ether</u>. To a mixture of 59.1g (0.1lm) of the potassium 2,2-dinitroethyl allyl ether and 200 ml of water was added 18.0g (0.15m) of 37% formaldehyde. Then 9.0g (0.15m) of acetic acid was added dropwise. The reaction mixture was stirred for an additional 15 minutes at ambient temperature and extracted with 3 x 33 ml of methylenechloride. The combined extracts were washed with 2 x 100 ml of water and concentrated to give 22.0g (97.1%) of light yellow liquid, $n_{25}D$ 1.4630.

Analysis: Calculated $C_6H_{10}N_2O_6$: C 34.96; H 4.89; N 13.59.
Found: C 34.27; H 5.30; N 12.84.

<u>3-Tosyl-2,2-dinitropropyl Allyl Ether</u>. A mixture of 4.0g (0.19m) of 3-hydroxy-2,2-dinitropropyl allyl ether, 4.0g (0.21m) of toluene sulfonyl chloride, and 20 ml of chloroform was heated to reflux with stirring and a solution of 2.0g (0.021m) of pyridine-N-oxide in 10 ml of chloroform was added dropwise in 50 minutes. The reaction mixture was refluxed for 114 hours, cooled, washed with water and then passed through a neutral alumina column to remove color and starting materials. The solution was concentrated to give 3.2g (65%) of a colorless oil, $n_{25}D$ 1.5100.

Analysis: Calculated $C_{13}H_{16}N_2O_8S$: C 43.33; H 4.48; N 7.77.
Found: C 43.24; H 4.90; N 7.22.

3-Azido-2,2-dinitropropyl Allyl Ether. A mixture of 4.0g (0.0112m) of 3-tosyl-2,2-dinitropropyl allyl ether, 1.2g (0.0185m) of sodium azide and 20 ml of dimethyl formamide was heated with stirring at 50 C for 90 hours. The mixture was cooled, poured into 100 ml of water, and extracted with 50 ml of methylene chloride. The organic extract was washed with 6 x 100 ml of water to remove the dimethyl formamide, passed through a neutral alumina column, and concentrated to give 0.6g (23%) of colorless oil, $n_{25}D$ 1.4768.

Analysis: Calculated $C_6H_9N_5O_5$: C 31.17, H 3.92.
Found: C 31.43; H 4.38.

3-Azido-2,2-dinitropropyl Glycidyl Ether. A mixture of 1.5g (0.0065m) of 3-azido-2,2-dinitropropyl allyl ether, 5g (0.035m) of disodium hydrogen phosphate, and 15 ml of methylene chloride was heated to reflux and a solution of 1.43g (0.011m) of freshly prepared peroxytrifluoroacetic acid in 5 ml of methylene chloride was added in 15 minutes. The reaction mixture was refluxed for an additional 2 hours, cooled, and 25 ml of water was added to dissolve all solids. The methylene chloride layer was separated and the aqueous layer was extracted with 2 x 10 ml of methylene chloride. The combined methylene chloride extracts were washed with 20 ml of 10% sodium bicarbonate solution, dried over anhydrous sodium sulfate, and concentrated to give 1.3g (81%) of yellow oil, $n_{23}D$ 1.4796.

Analysis: Calculated for $C_6H_9N_5O_6$: C 29.16; H 3.67; N 28.33.
Found: C 29.07; H 3.71; N 28.12

SYNTHESIS AND CHARACTERIZATION OF THE POLYMER OF
3,3-BIS(AZIDOMETHYL) OXETANE (BAMO)

The objectives of this study were to:

1. Determine the feasibility of polymerizing BAMO
2. Obtain a BAMO polymer with the following properties
   a. Molecular weight range of 2000 to 4000
   b. A narrow molecular weight distribution
   c. A functionality (hydroxyl content) or 2 or more.

Parameters examined in these studies included:

1. Type and amount of solvent employed
2. Reaction stoichiometry, i.e., the relative concentration of monomer, catalyst and chain terminator
3. The nature of the chain termination.

Throughout this study, BF_3·etherate was employed as the catalyst with either water or glycerol as the chain terminator. Experimental techniques employed in both the synthesis and characterization efforts are described in the experimental section. All polymerization experiments are described in Table 3. Figures of the molecular weight distribution chromatograms are included for illustrative experiments.

Water as the Terminating Species

Halogenated solvents (carbon tetrachloride, chloroform, and methylene chloride) as well as nitromethane were examined. The former had been employed as the reaction medium in preparation of poly (glycidyl fluorodinitroethoxide) while the latter has been reported as favorably affecting the polymerization of oxetanes because of the high dielectric value. Polymerization occurred in all these media. In both carbon tetrachloride and nitromethane, the polymer precipitated during the reaction. Nitromethane and carbon tetrachloride gave either very broad molecular weight distribution or (with excess water) very low molecular weight.

TABLE 3. POLYMERIZATION OF 3,3-BIS(AZIDOMETHYL) OXETANE

Experiment No.	Oxetane (mole)	H_2O (mole)	Glycerol (mole)	$BF_3 \cdot$ etherate (mole)	Solvent Volume	Solvent
6	0.024	0	0	(1ml)	20 ml	CH_3NO_2
10	0.024	0.0056	0	(1ml)	20 ml	CH_3NO_2
11	0.024	0.056	0	(1ml)	20 ml	CH_3NO_2
62	0.012	0.006	0	0.006	25 ml	CCl_4
63	0.012	0.009	0	0.006	25 ml	CCl_4
64	0.012	0.006	0	0.006	25 ml	CH_2Cl_2
65	0.012	0.009	0	0.006	25 ml	CH_2Cl_2
66	0.012	0.009	0	0.006	15 ml	CH_2Cl_2
64A	0.012	0.003	0	0.006	15 ml	CH_2Cl_2
64C	0.012	0.009	0	0.006	10 ml	CH_2Cl_2
64D	0.012	0.009	0	0.006	10 ml	CCl_4
64R	0.012	0.009	0	0.006	15 ml	CH_2Cl_2
65A	0.012	0.015	0	0.006	15 ml	CCl_4
66A	0.012	0.009	0	0.006	15 ml	$CHCl_3$
66B	0.012	0.015	0	0.006	15 ml	$CHCl_3$
66C	0.012	0.015	0	0.006	10 ml	$CHCl_3$
66D	0.012	0.009	0	0.006	10 ml	$CHCl_3$
101	0.006	0	0.0045	0.003	5 ml	CH_2Cl_2
102	0.006	0	0.0045	0.003	5 ml	$CHCl_3$
105	0.006	0	0.0025	0.003	5 ml	CH_2Cl_2
106	0.006	0	0.006	0.003	5 ml	CH_2Cl_2
101A	0.006	0	0.0045	0.003	5 ml	CH_2Cl_2
107	0.006	0	0.0045	0.006	5 ml	CH_2Cl_2
101A-10X	0.06	0	0.045	0.03	50 ml	CH_2Cl_2
107-10X	0.06	0	0.045	0.06	50 ml	CH_2Cl_2

The polymer obtained (Run 62) was so high in molecular weight (>4000) that it was
deemed impractical for use as a binder. Addition of more water (Run 63) did lower
the molecular weight but not sufficiently to bring it to the desired range. A
further increase in water content (Run 65A) did bring the polymer within the
range desired; however, a very broad molecular weight distribution (Fig. 1) was
obtained. It was therefore concluded to reject carbon tetrachloride as a solvent
for a similar reason to nitromethane, in that too wide a distribution was obtained.

Both in methylene chloride and chloroform, polymers in the proper molecular weight range and with a narrow distribution were obtained which did not precipitate in the reaction medium (Runs 64C, 66D, Fig. 2 and 3). Regardless of the solvent ($CHCl_3$ or CH_2Cl_2), polymerization in a more concentrated medium resulted in a narrower molecular weight distribution; for example, Runs 65 and 64R, Runs 66A and 66D.

Concentration of Water

The key to molecular weight control in BAMO polymerization is the amount of water in the medium. Thus, when Runs 64R, 64A, and 64C are compared (Fig. 4, 5 and 2), it can be seen that increasing water content has a significant impact on the range obtained and is only minimally affected by the relative concentration of solvent.

Functionality of BAMO

Having established that a BAMO polymer can be obtained in the desired molecular weight range and with a narrow molecular weight distribution, the functionality (see Experimental Section for the method employed) of Run 64C was determined to be only 1.7. This points up a fundamental difficulty in the system using water as a chain terminator. In Fig. 6, the various means of chain termination are illustrated. When water is effective (i.e., no alternative routes occur), a functionality no greater than two results. In the presence of anionic contamination or when termination is by disproportionation, the overall product must be less than bifunctional. Such material would behave poorly as a binder in that satisfactory crosslinking could not be obtained. Because this problem always exists in an oxetane polymerization where water is used to stop the chain growth, it makes this approach replete with difficulties. By contrast, when glycerol is used in place of water, a trifunctional product is obtained (Fig. 7). Thus, even if the side reactions (contaminants, disproportionation) occur, the functionality will never drop below 2 and a polymer which can perform successfully as a cross-linkable binder will always be obtained. For this reason, the replacement of water by glycerol was made and all subsequent studies involve this system.

Glycerol as a Chain Terminator

The influence of solvent in this system was compared in Runs 101A and 102 (Fig. 8 and 9). It appears that methylene chloride gives a somewhat narrower distribution than does chloroform. For this reason the former was used throughout the subsequent experiments described below. Runs 105 and 106 were to determine the influence of changes in glycerol concentration on the molecular weight of BAMO polymer obtained. It is interesting to note that, regardless of the glycerol content, the polymer obtained had essentially the same molecular weight. A possible explanation of the result is the observation that in all the glycerol-containing reactions, the bulk of the glycerol separated from the methylene chloride solution. Thus, it would appear that the actual concentration of glycerol available in the medium is far lower than that added and therefore at this low concentration, additional glycerol has no effect on the molecular weight. A more efficient means for molecular weight control in this system is via the BF_3·etherate catalyst concentration. Thus, in Run 107 (Fig. 10) where the catalyst is doubled over that of 101A, the molecular weight was substantially reduced.

Having established that a polymer in the desired 2000 to 4000 range with a narrow molecular weight distribution could be obtained in this system, the typical 1 gram reaction was scaled up to the 10 gram level to provide sufficient polymer to determine functionality and curing behavior (Runs 101A-10X and 107-10X). With the scaleup, for the first time, a significant polymerization exotherm was observed (the temperature rose approximately 15 C). This resulted in a change in the molecular weight distribution. Compare Fig. 8 for 101A with Fig. 11 for 101A-10X and Fig. 10 for 107 with Fig. 12 for 107-10X. It can be seen that there is a slight reduction in molecular weight and the appearance of a fraction with an approximate DF-4. This new peak may result either from the influence of the exotherm or may be evidence of the presence of a tetramer which has been reported for oxetane polymers. Regardless of the somewhat changed polymer molecular weight and distribution for the scaled-up runs, the polymer range and narrow distribution warranted determination of both functionality and curing behavior.

Both prepolymers cured well and gave tough gumstocks. Data are given in Table 4. From the experiments described above, it can be concluded that several of the objectives have been achieved:

1. The feasibility of obtaining a BAMO polymer
2. Producing a BAMO polymer in the 2000 to 4000 molecular weight range with a narrow distribution and functionalities greater than two
3. The ability to scaleup the reaction from the 1 to 10 gram level without a drastic change in the product obtained.

What remains to be done in a subsequent study is to obtain a better understanding of:

1. The termination reaction when glycerol is employed
2. The influence of temperature on molecular weight and molecular weight distribution
3. The ease of reproducibility of the scaleup reaction

TABLE 4.   CURE OF BAMO POLYMERS

Sample	Weight Average, Molecular Weight, ($\bar{M}_w$)	Hydroxyl Equivalent Weight	Functionality	Sample Weight, grams	Sample Hydroxyl Meq.	HMDI Meq	DBTDL Catalyst
101A-10X	2920	1050	2.8	4.70	4.5	4.7	1 drop
107-10X	2037	680	3.0	2.06	3.0	3.3	1 drop

Experimental Details

Synthesis. The majority of the experiments were performed on a micro scale using 1 or 2 grams of oxetane monomer. In early runs, the oxetane monomer, chain terminator (water or glycerol), and solvent were placed in a small flask and stirred with a magnetic stirrer. The catalyst ($BF_3 \cdot Et_2O$) was added with stirring, and the polymerization reaction was allowed to proceed at room temperature with stirring for approximately 2 to 3 hours.

The excess solvent was allowed to evaporate at room temperature. The residue was washed with hexane, air dried, then dissolved in tetrahydrofuran, dried over $MgSO_4$ for several hours, filtered, and the tetrahydrofuran was evaporated to obtain the polymeric product.

In later experiments (designated as 100 series), the solvent and chain terminator were placed in a small flask, the catalyst was added with stirring then the oxetane monomer was added slowly with stirring. The polymerization was allowed to proceed at room temperature (no temperature controls) with stirring for approximately 3 hours. Then a few milliliters of concentrated ammonium hydroxide solution were added to destroy the catalyst complex. The solvent was evaporated under vacuum, the residue was washed with water, then with a small amount of methanol, then dried under vacuum, dissolved in methylene chloride, dried over $MgSO_4$, filtered, and the methylene chloride was evaporated under vacuum to yield a solid polymer, which melted in the range of 73 to 78 C.

Two reactions, 101A-10X and 107-10X, were scaled up by a factor of 10. For these experiments, the $BF_3 \cdot Et_2O$ and oxetane monomer were added alternately in small amounts until all the reactants were added. The temperature rose initially in these larger scale experiments and yielded a broader molecular weight distributions and slightly lower average molecular weight then the similar micro-scale experiments. This means that the temperature effect must be studied and provision made for controlling the temperature at the optimum for the desired product characteristics.

Molecular Weight Determination. The samples were dissolved in chromatographic grade tetrahydrofuran (THF) at a concentration of 5 mg/ml. The molecular weight separation was obtained using two Dupont SE60 $\overset{o}{A}$ porous silica size exclusion columns with a THF solvent flowrate of 1 ml/min on a Spectra-physics 3500B liquid chromatograph. Sample detection was made with a Waters Associates Model 401 differential refractometer. The sample size was 100 µl. The calibration curves were obtained using polypropylene glycol standards of molecular weight 4000, 2000, 1200 and 800 (Waters Associates).

The calibration curves (which should be matched to the chromatograms according to experimental date), are Fig. 13 to 16.

Functionality. Hydroxyl equivalent weights were determined using a recently developed method by AFRPL Chemical Branch*. Functionality is calculated by dividing the weight average molecular weight, $\overline{Mw}$, by the hydroxyl equivalent weight.

Curing Studies. Using molecular weight and hydroxyl equiv lent weight data, polymers were cured using hexamethylene-diisocyanate (HMDI) and dibutyltindi-laurate (DBTDL) catalyst. The solid polymer samples were dissolved in 1,2-dichloroethane solvent and mixing was by hand under nitrogen atmosphere within a glove box. After 48 hours, remaining solvent was removed from cured samples at 45 C.

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*Dee, L. A. et al., Use of N-methylimidazole as a Catalyst for Acetylation of Hydrosyl Terminated Polymers, AFRPL Chemical Branch, LKLR, Edwards, California, 93523.

DATE: Nov 19, 1979

SAMPLE: 65A/CCl$_3$

ELUTION VOLUME, ARBITRARY UNITS
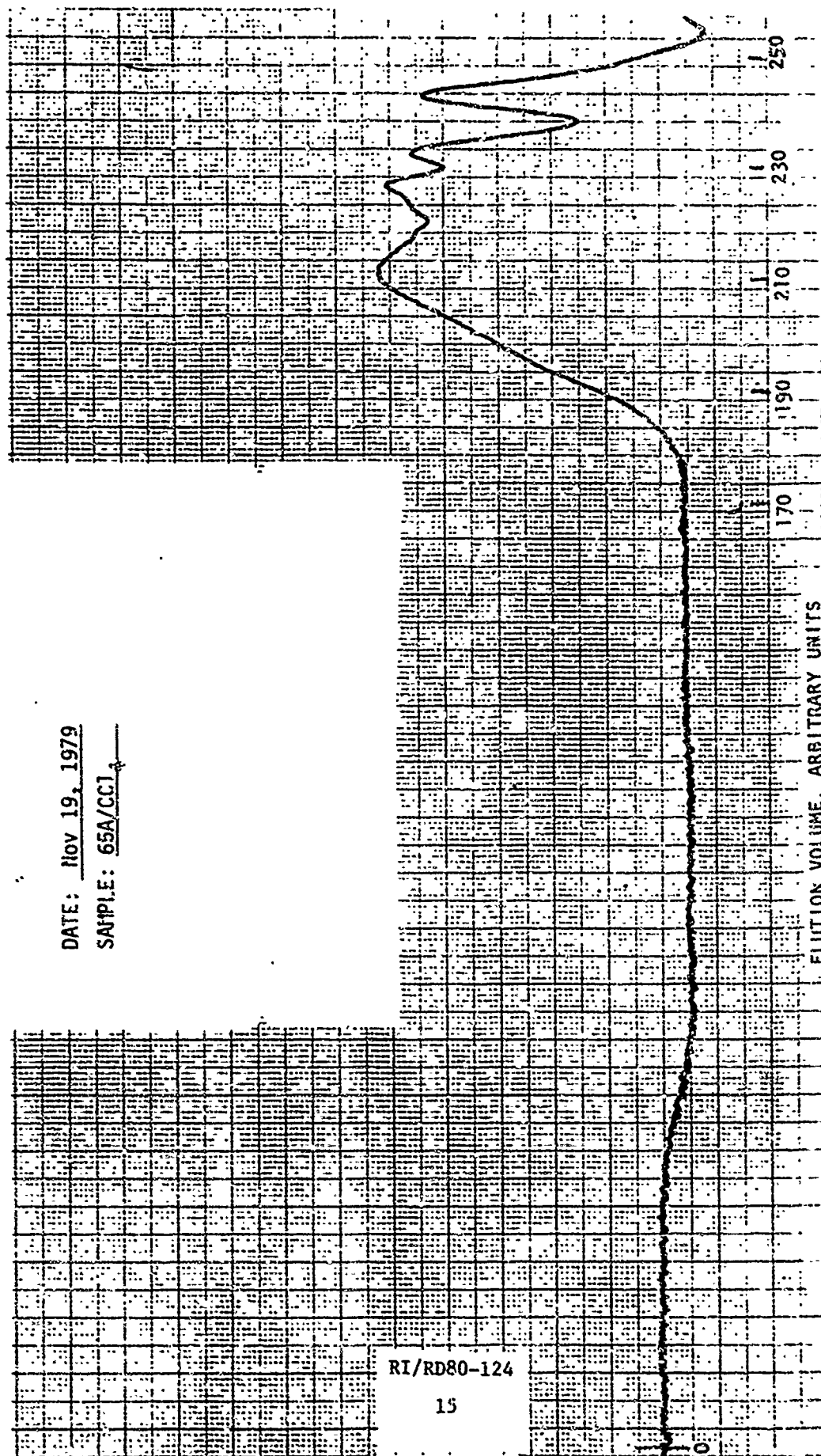
Figure 1. The Size Exclusion Chromatogram of Sample 65A
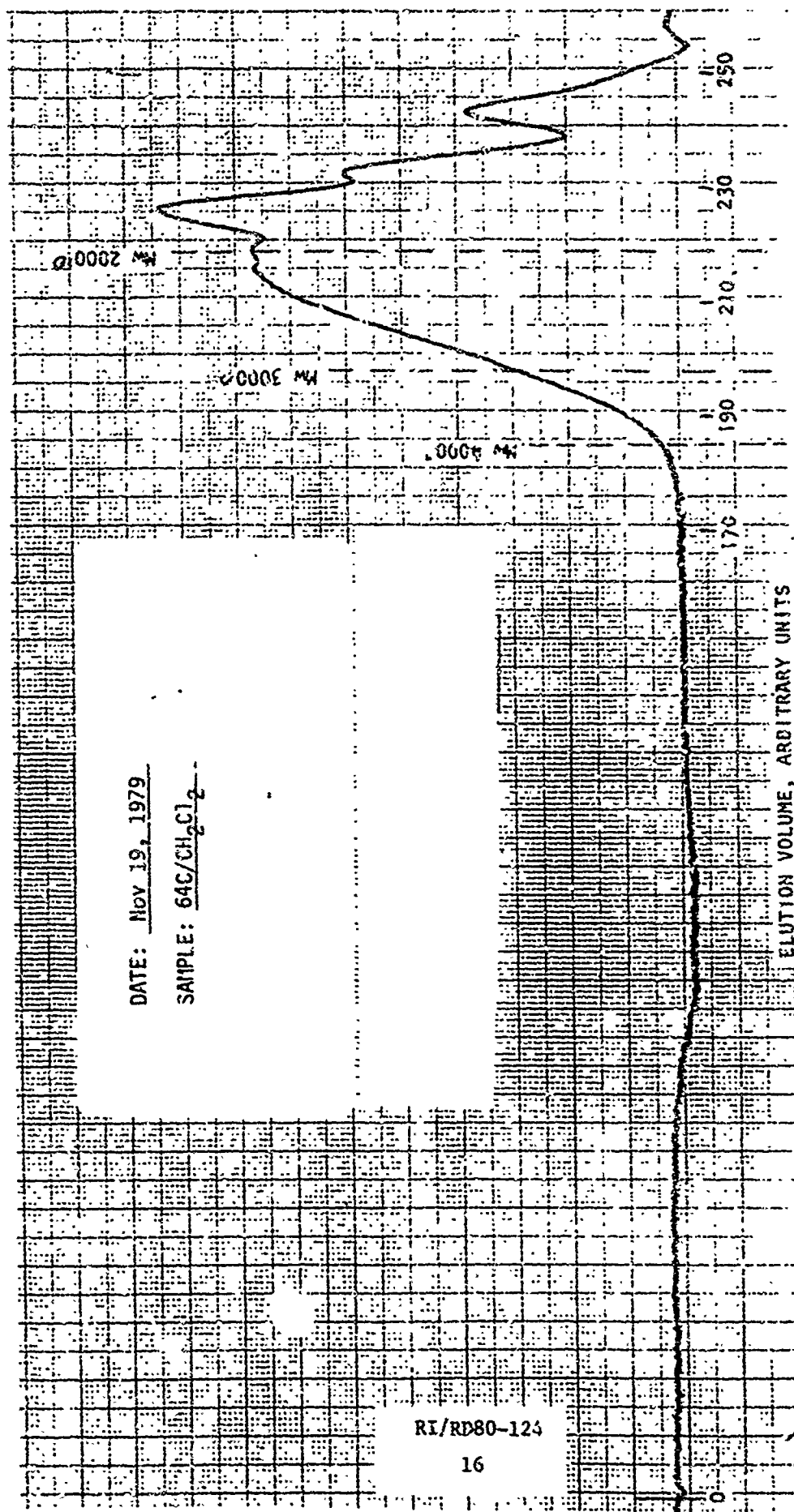
Figure 2. The Size Exclusion Chromatogram of Sample 64C

DATE: Nov 19, 1979

SAMPLE: 64C/CH₂Cl₂

ELUTION VOLUME, ARBITRARY UNITS

DATE: Nov 19, 1979

SAMPLE: 660/CHCl$_3$

ELUTION VOLUME, ARBITRARY UNITS
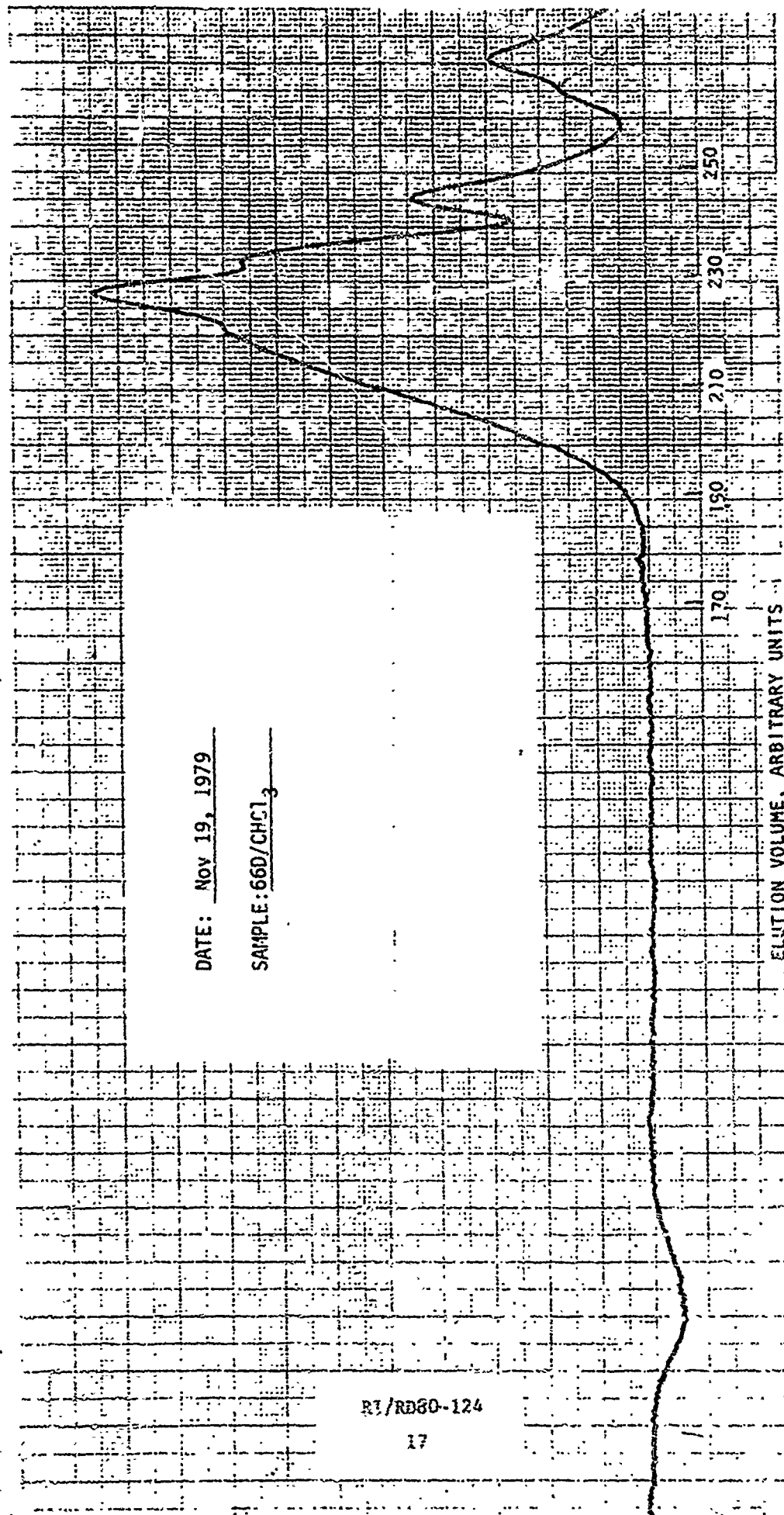
Figure 3. The Size Exclusion Chromatogram of Sample 660

DATE: Nov 19, 1979

SAMPLE: 64R/CH$_2$Cl$_2$
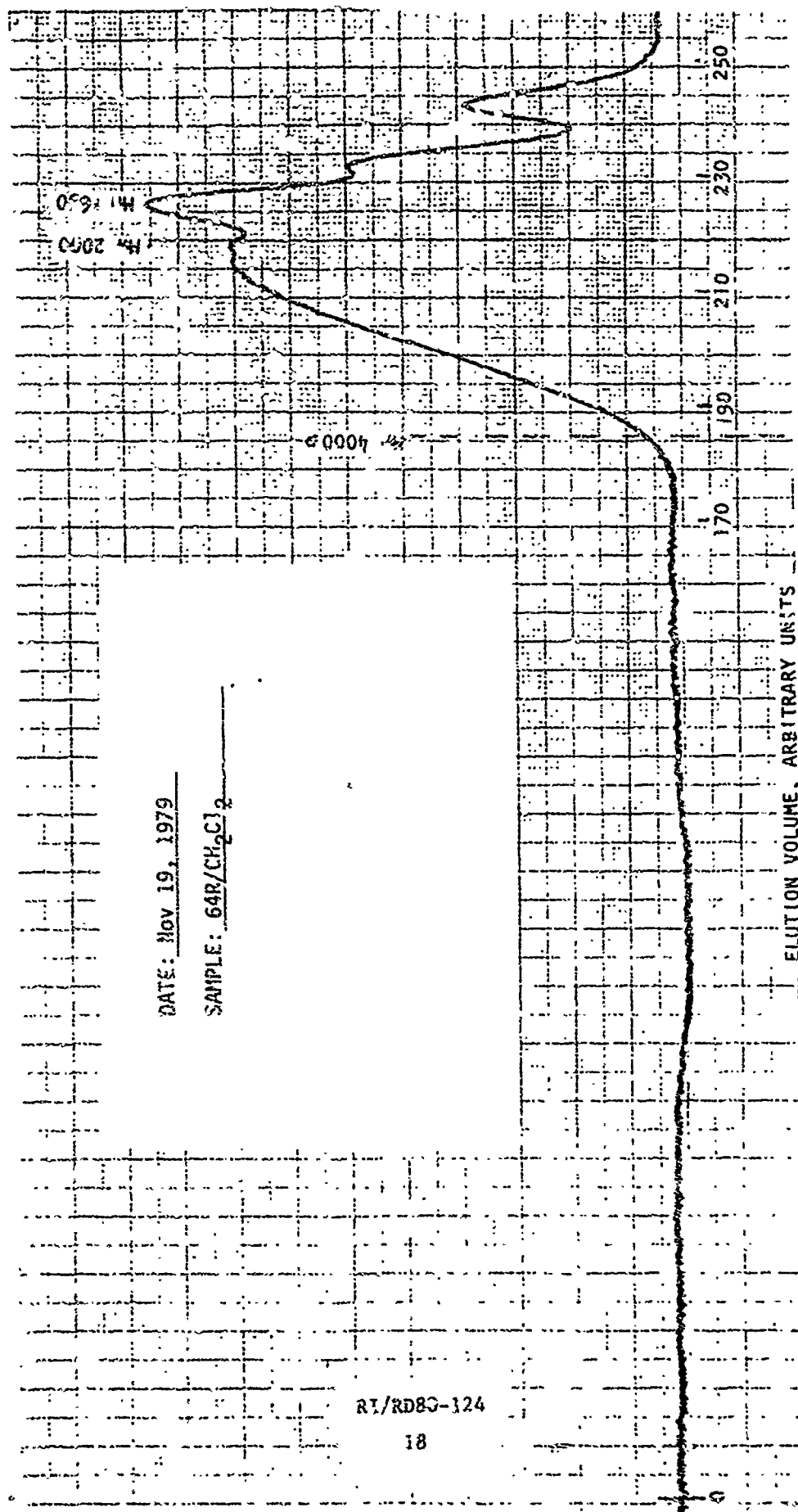
M̄$_w$ 4000

M̄$_w$ 2050

M̄$_w$ 1650

ELUTION VOLUME, ARBITRARY UNITS

Figure 4. The Size Exclusion Chromatogram of Sample 64R
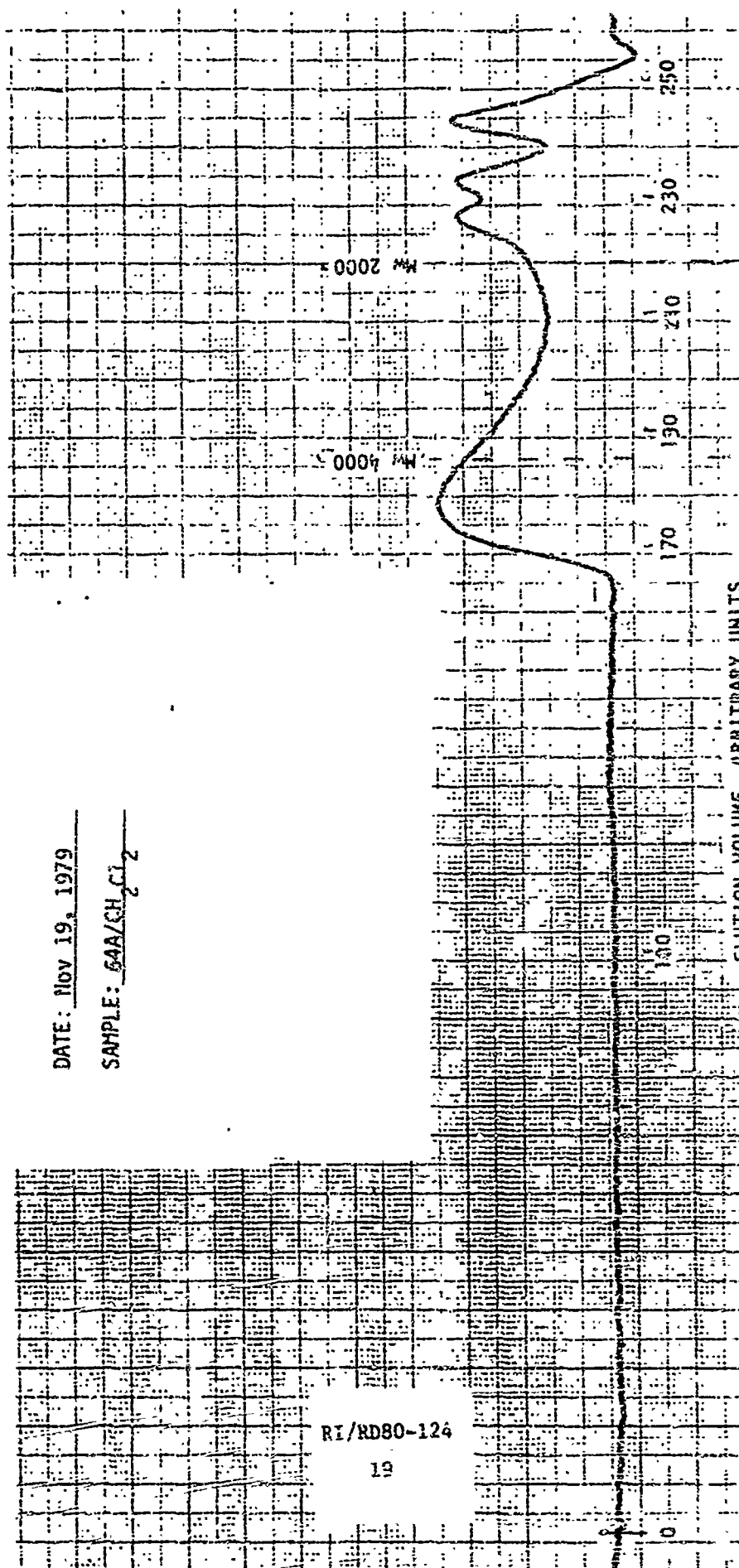
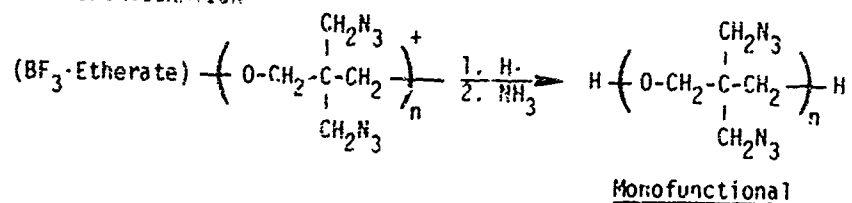Figure 5. The Size Exclusion Chromatogram of Sample 64A

1. ANIONIC CONTAMINANTS

$$(BF_3 \cdot Etherate) - \left(O-CH_2-\underset{\underset{CH_2N_3}{|}}{\overset{\overset{CH_2N_3}{|}}{C}}-CH_2 \right)_n^+ \xrightarrow[2.\ NH_3]{1.\ Y^-} H \left(O-CH_2-\underset{\underset{CH_2N_3}{|}}{\overset{\overset{CH_2N_3}{|}}{C}}-CH_2 \right)_n Y$$

<u>Monofunctional</u>

2. DISPROPORTIONATION

$$(BF_3 \cdot Etherate) - \left(O-CH_2-\underset{\underset{CH_2N_3}{|}}{\overset{\overset{CH_2N_3}{|}}{C}}-CH_2 \right)_n^+ \xrightarrow[2.\ NH_3]{1.\ H\cdot} H \left(O-CH_2-\underset{\underset{CH_2N_3}{|}}{\overset{\overset{CH_2N_3}{|}}{C}}-CH_2 \right)_n H$$

<u>Monofunctional</u>

3. WATER

$$(BF_3 \cdot Etherate) - \left(O-CH_2-\underset{\underset{CH_2N_3}{|}}{\overset{\overset{CH_2N_3}{|}}{C}}-CH_2 \right)_n^+ \xrightarrow[2.\ NH_3]{1.\ H_2O} H \left(C-CH_2-\underset{\underset{CH_2N_3}{|}}{\overset{\overset{CH_2N_3}{|}}{C}}-CH_2 \right)_n OH$$

<u>Difunctional</u>
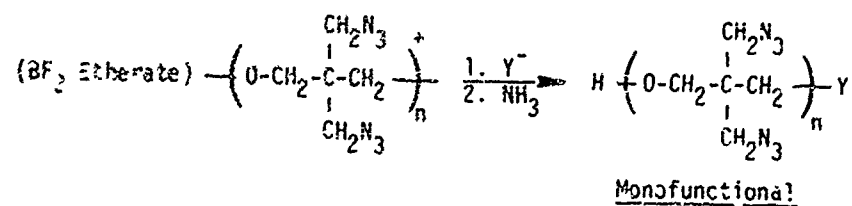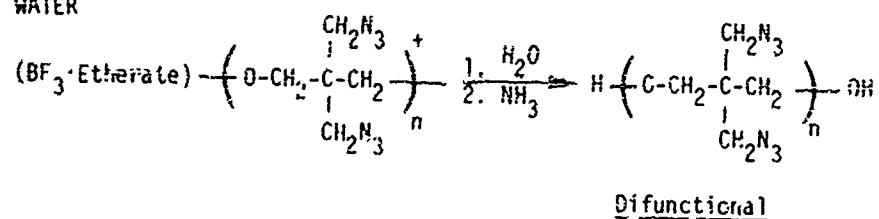
Figure 6. Chain Termination of Oxetane Polymerization

$$(BF_3 \cdot Etherate) - \left(O-CH_2-\underset{\underset{CH_2N_3}{|}}{\overset{\overset{CH_2N_3}{|}}{C}}-CH_2 \right)_n^+ + HO-CH_2-CHOH-CH_2-OH \longrightarrow$$

$$H \left(- O-CH_2-\underset{\underset{CH_2N_3}{|}}{\overset{\overset{CH_2N_3}{|}}{C}}-CH_2 \right)_n O-CH_2-CH-CH_2-O \left(CH_2-\underset{\underset{CH_2N_3}{|}}{\overset{\overset{CH_2N_3}{|}}{C}}-CH_2-O \right)_n H$$

$$\underset{\underset{CH_2N_3}{|}}{\overset{O}{|}} \left(CH_2-\overset{|}{\underset{|}{C}}-CH_2-O \right)_n H$$

or

$$H \left(O-CH_2-\underset{\underset{CH_2N_3}{|}}{\overset{\overset{CH_2N_3}{|}}{C}}-CH_2 \right)_n O - CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-O - \left(CH_2-\underset{\underset{CH_2N_3}{|}}{\overset{\overset{CH_2N_3}{|}}{C}}-CH_2-O \right)_n H$$
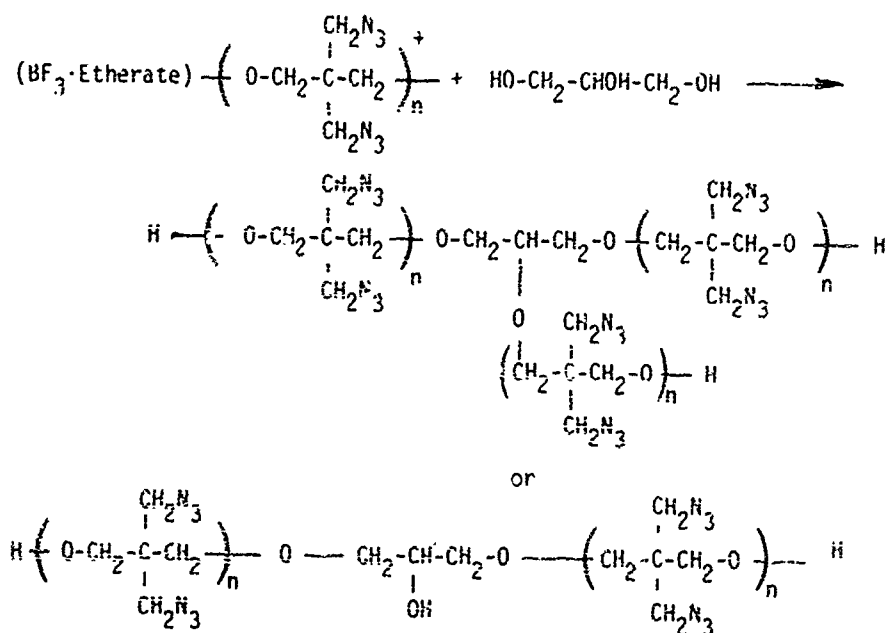
Figure 7. Chain Termination by Glycerol
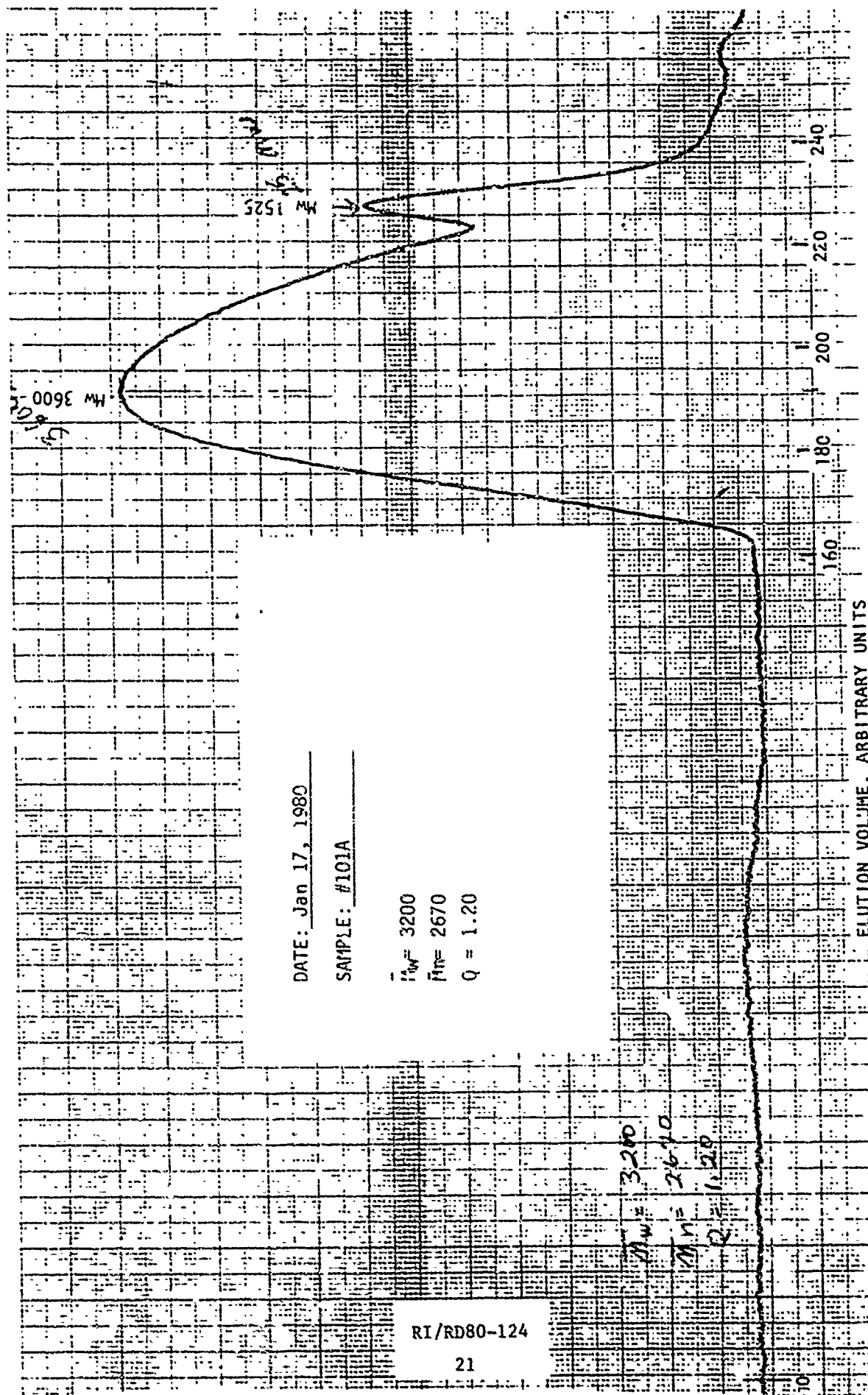
Figure 8. The Size Exclusion Chromatogram of Sample 101A

DATE: Jan 17, 1980

SAMPLE: #101A

$\bar{M}_w$ = 3200
$\bar{M}_n$ = 2670
Q = 1.20

MW 3600

MW 1525

ELUTION VOLUME, ARBITRARY UNITS

240   220   200   180   160

RI/RD80-124

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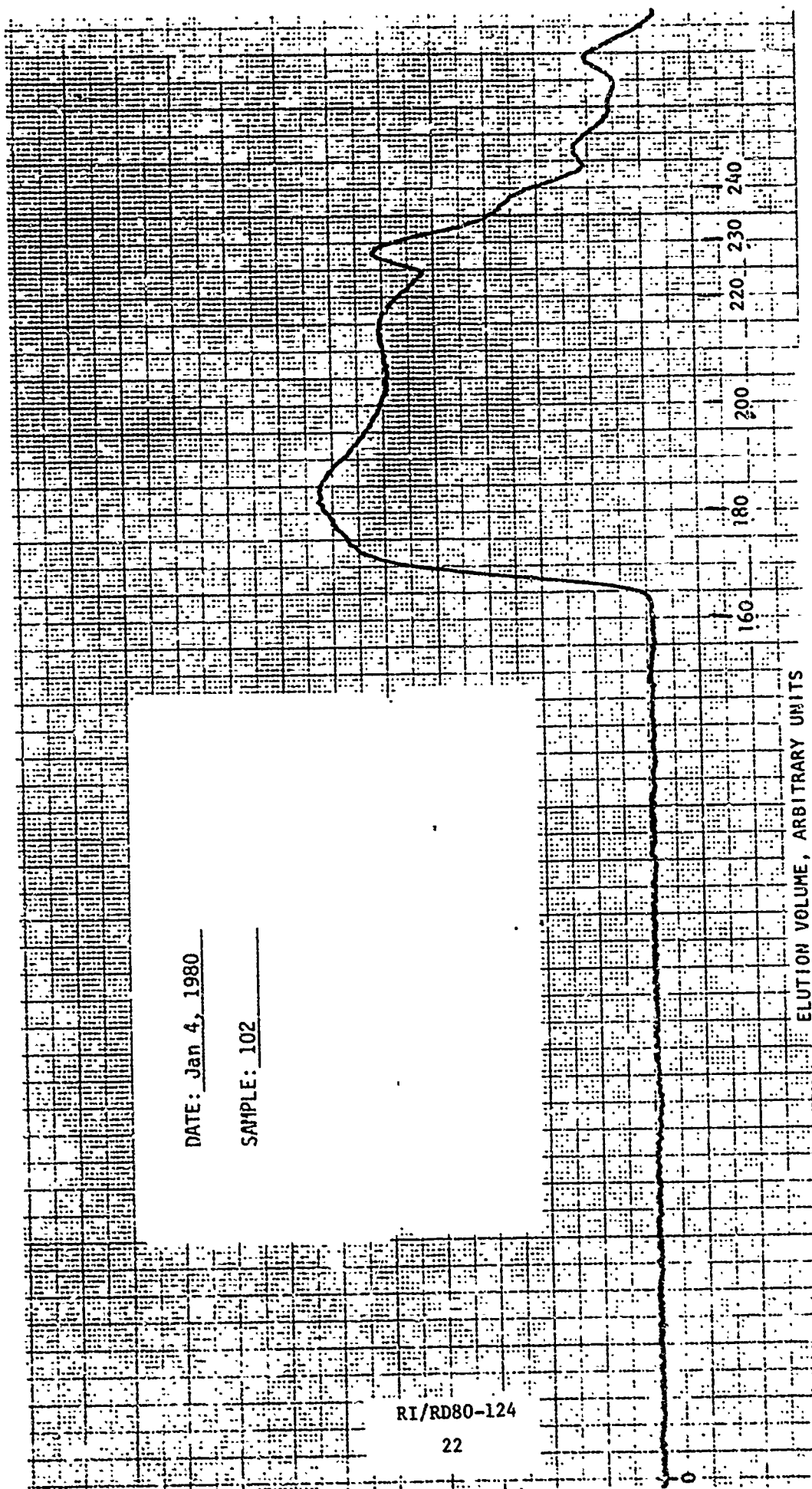
Figure 9. The Size Exclusion Chromatogram of Sample 102

DATE: Jan 4, 1980

SAMPLE: 102

ELUTION VOLUME, ARBITRARY UNITS
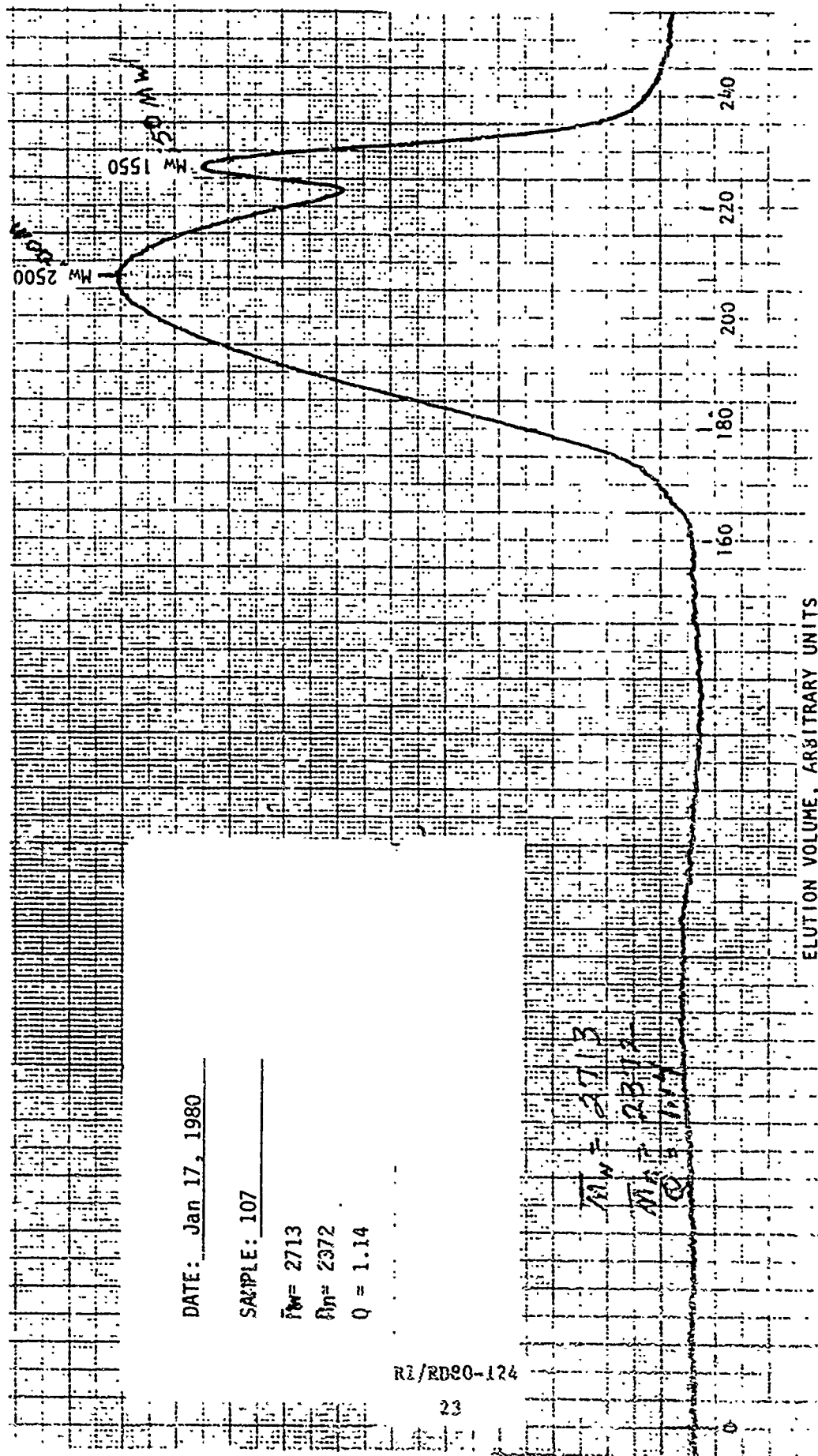
Figure 10. The Size Exclusion Chromatogram of Sample 107

DATE: Jan 17, 1980

SAMPLE: 107

$\bar{M}_w$ = 2713
$\bar{M}_n$ = 2372
Q = 1.14

$\bar{M}_w$ = 2713
$\bar{M}_n$ = 2311.3
Q = 1.14

MW 2500

MW 1550

50 MW

ELUTION VOLUME, ARBITRARY UNITS

240   220   200   180   160

RI/RD80-124

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Figure 11. The Size Exclusion Chromatogram of Sample 101A-10X

DATE: Feb 4, 1980

SAMPLE: 101A-10X

$\bar{M}_w$= 2920
$\bar{M}_n$= 2237
Q = 1.31

Mw 4000

Mw 1550

Mw 780

ELUTION VOLUME, ARBITRARY UNITS

$\bar{M}_w = 2920$
$\bar{M}_n = 2237$
$Q = 1.31$

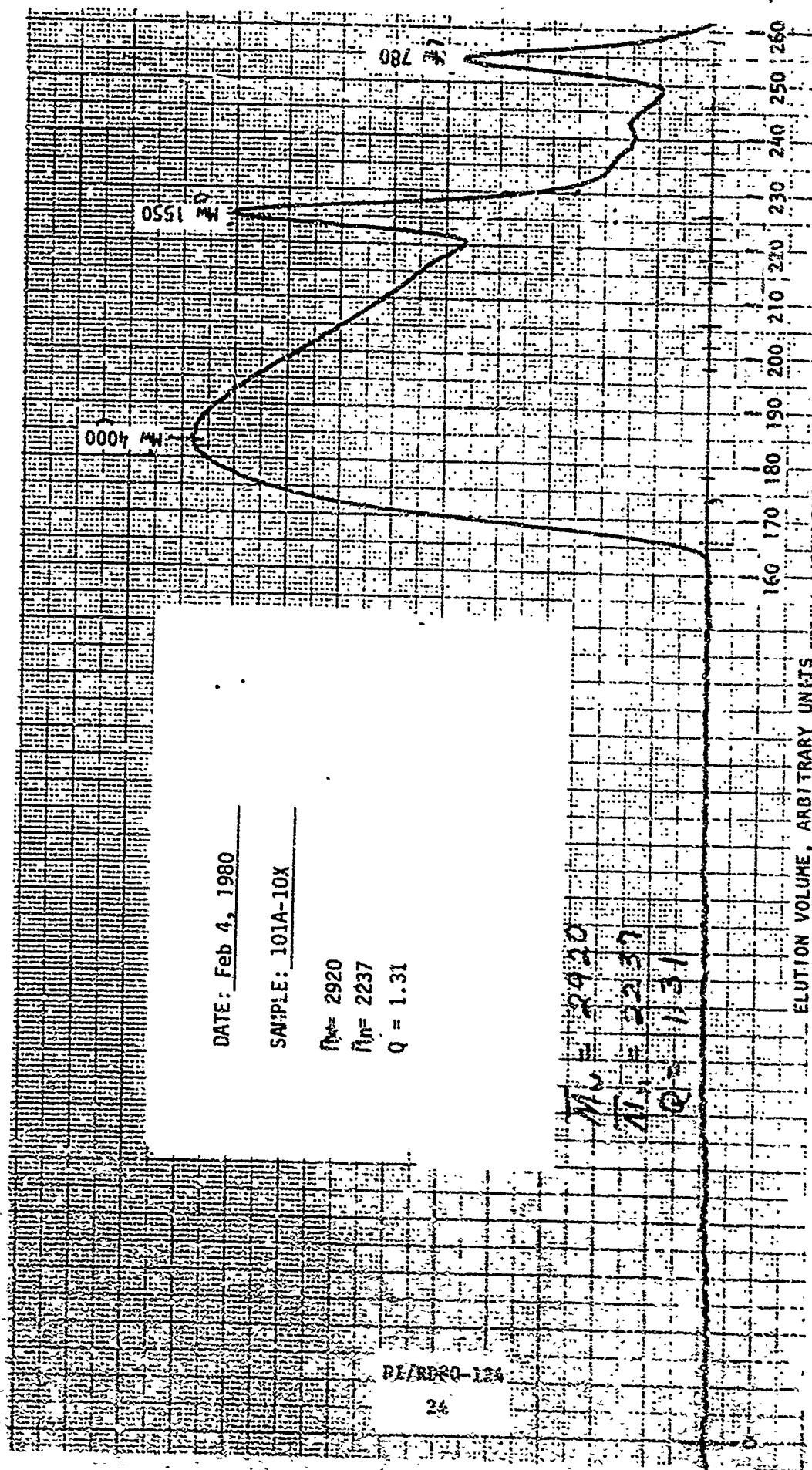160 170 180 190 200 210 220 230 240 250 260

Figure 12. The Size Exclusion Chromatogram of Sample 107-10X

DATE: ___Feb 4, 1980___

SAMPLE: ___107-10X___
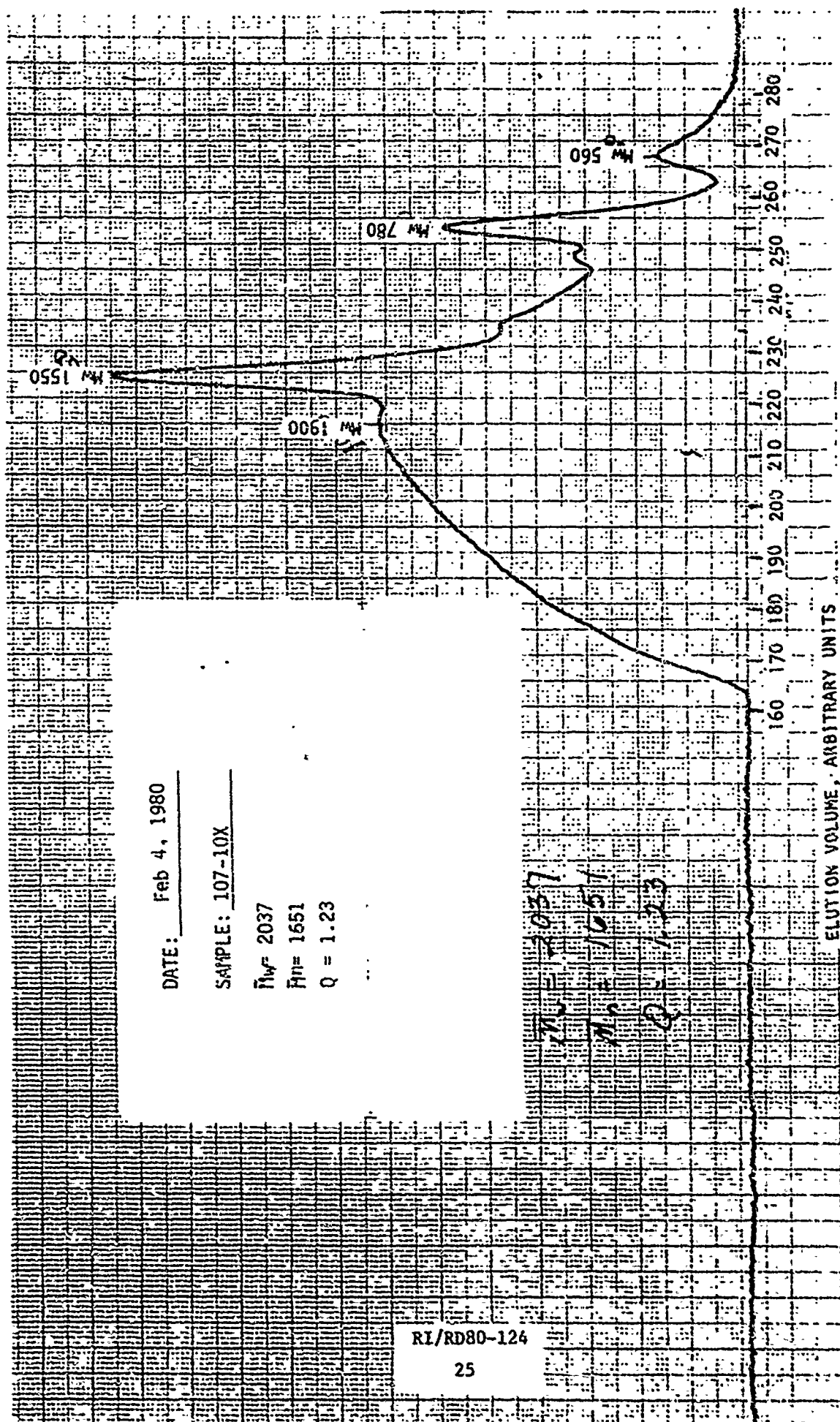
$\bar{M}_w$ = 2037
$\bar{M}_n$ = 1651
Q = 1.23
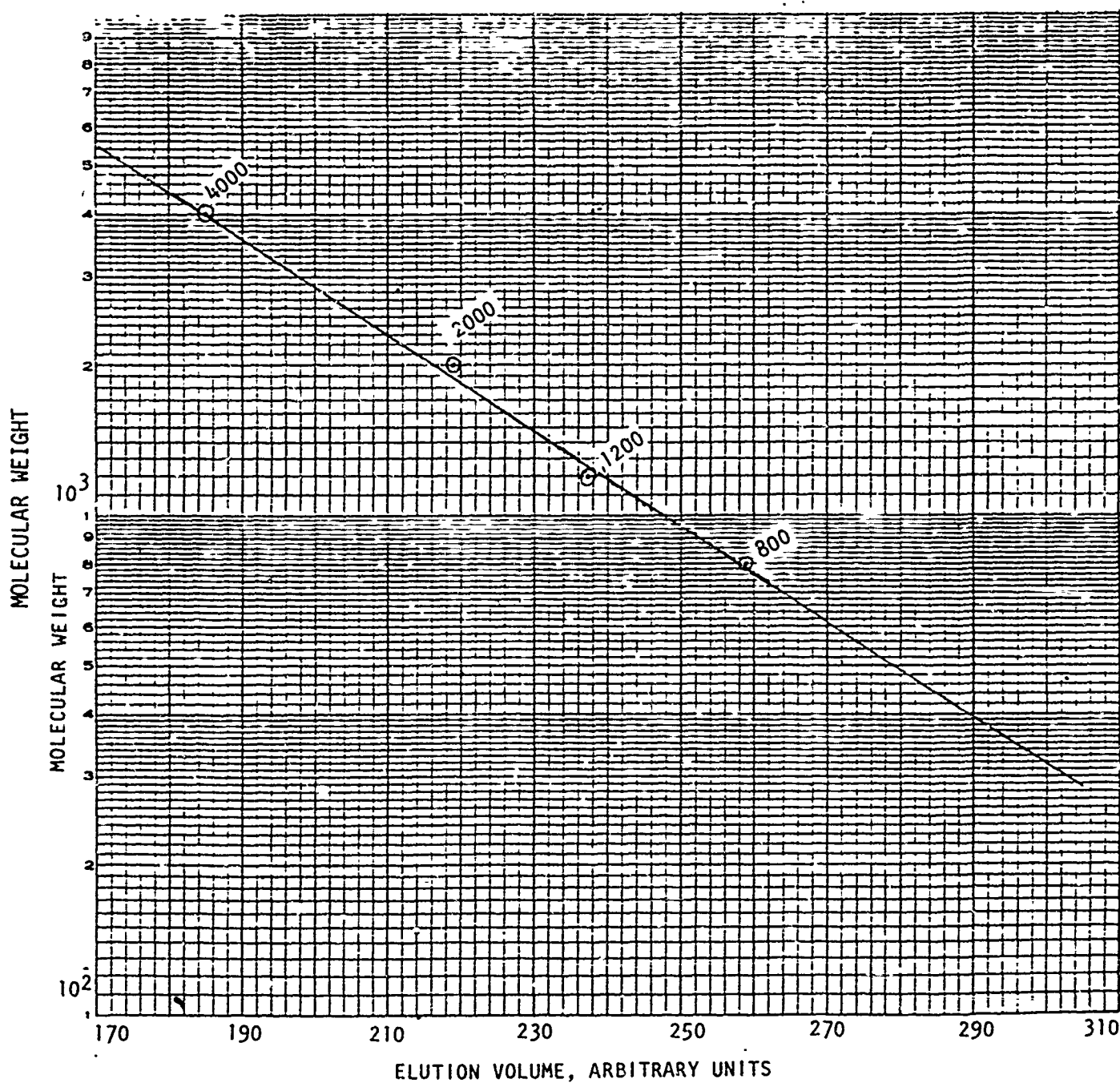
ELUTION VOLUME, ARBITRARY UNITS

Figure 13. Calibration Curve of Molecular Weight vs Elution Volume
for Polypropylene Glycol Standards 11/19/79

Figure 14. Calibration Curve of Molecular Weight vs Elution Volume
for Polypropylene Glycol Standards 01/04/80
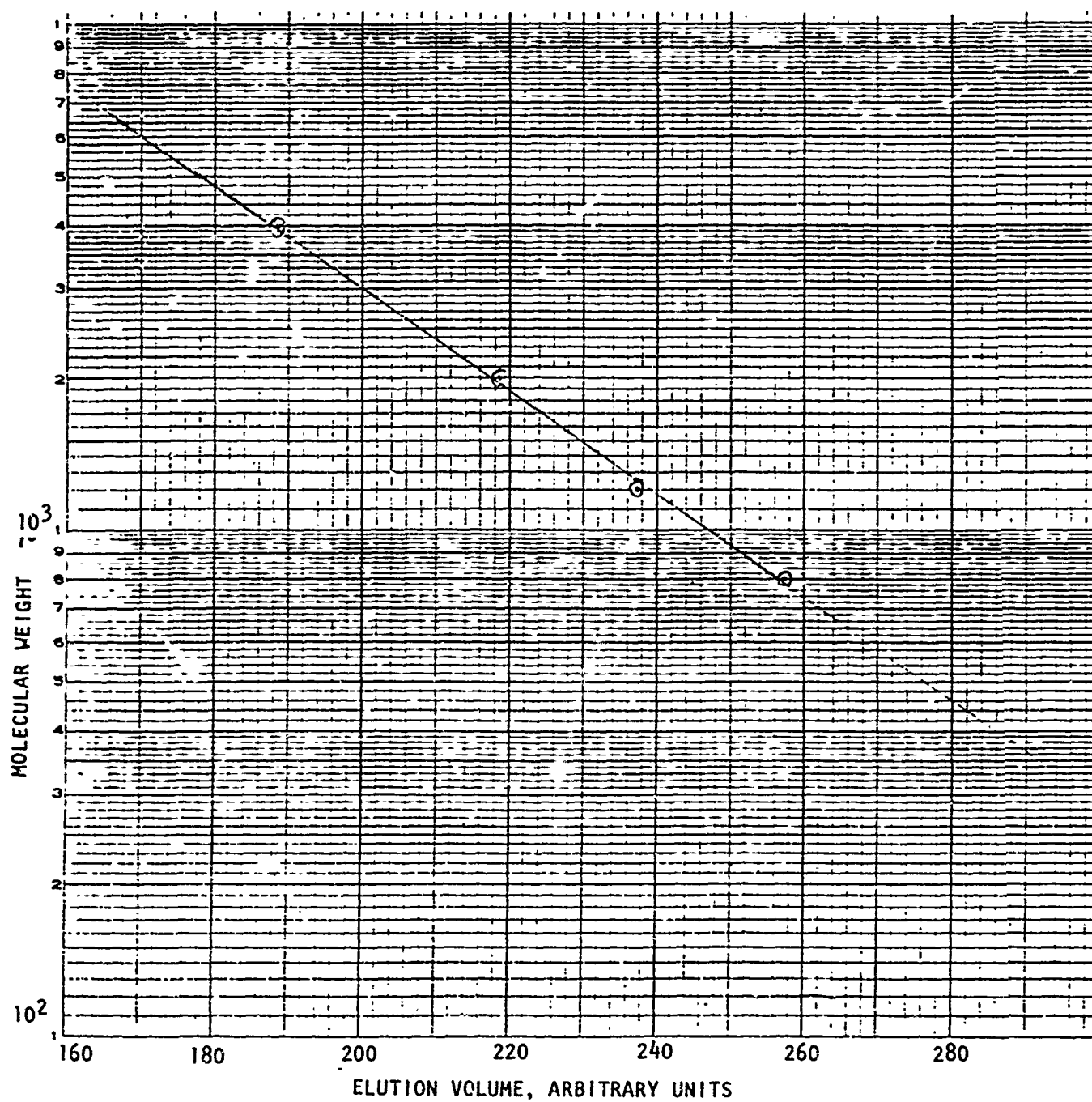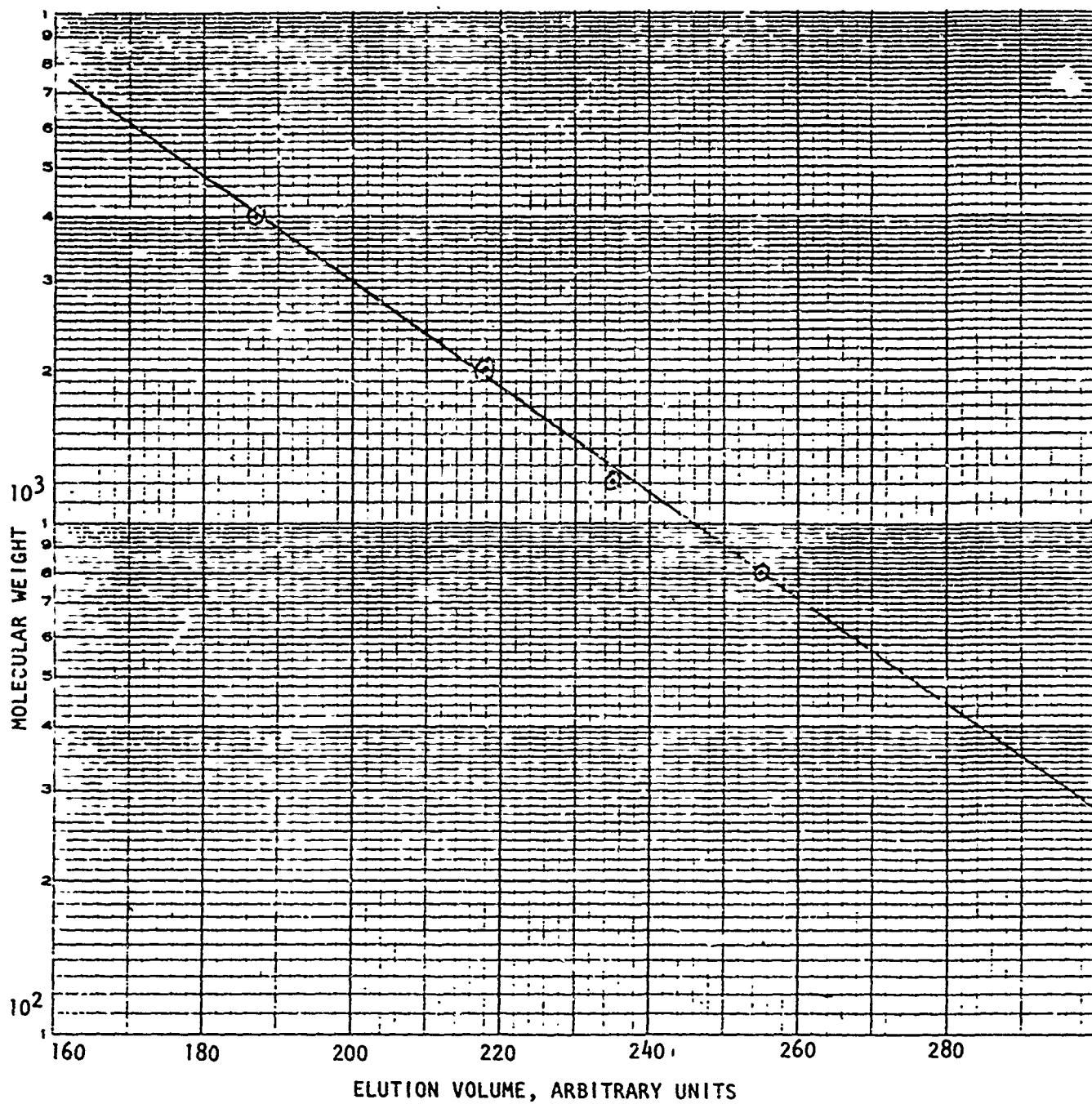
RI/RD80-124

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Figure 15. Calibration Curve of Molecular Weight vs Elution Volume
for Polypropylene Glycol Standards 01/17/80

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Figure 16. Calibration Curve of Molecular Weight vs Elution Volume
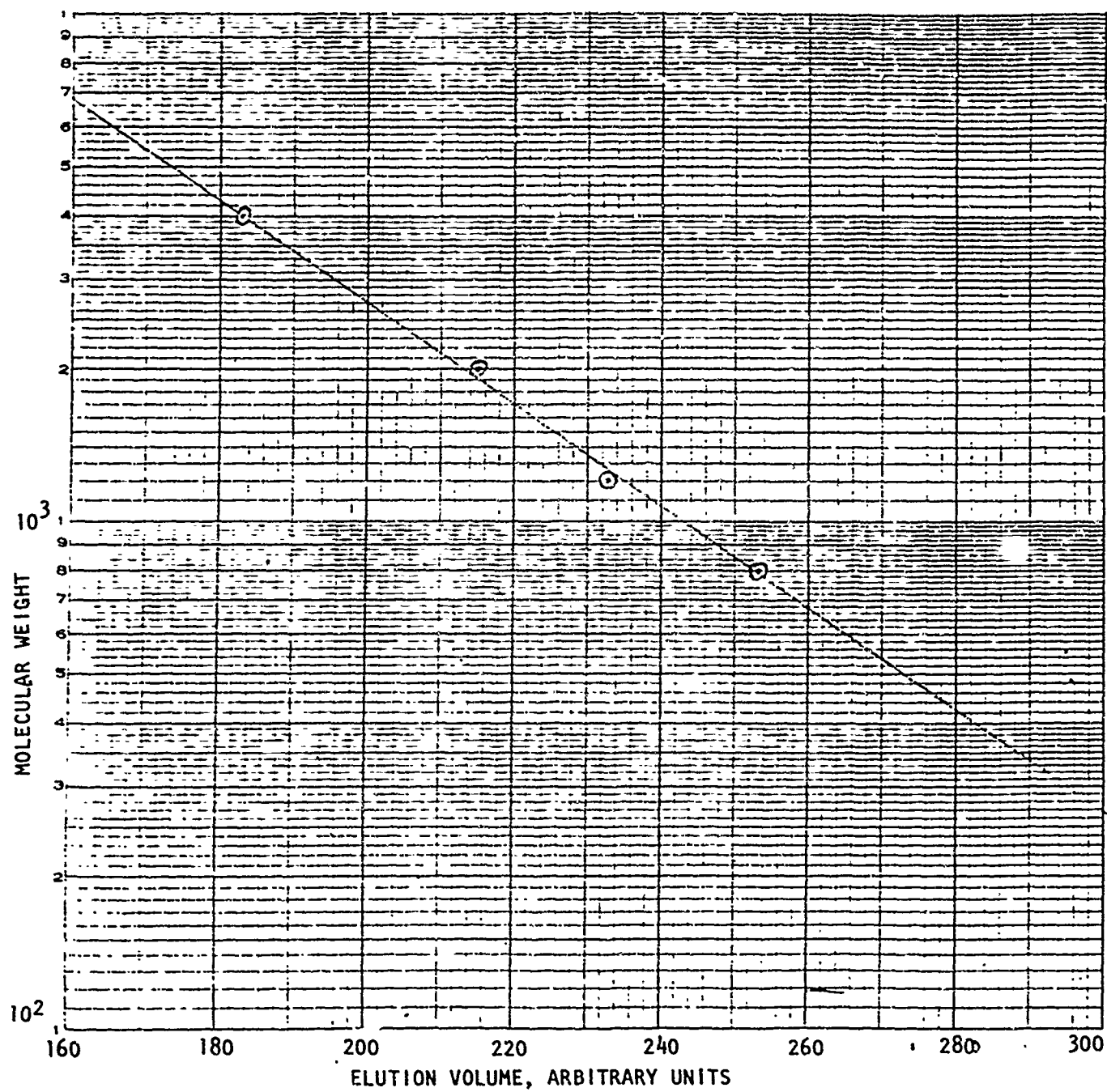for Polypropylene Glycol Standards 02/04/80

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